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GTI PROJECT NUMBER 20750

Feasibility of Using Plastic Pipe for Ethanol Gathering

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Results and Conclusions

All the steering committee feedback on the background ethanol information from the 1st Quarter project report was incorporated and the updated sections from that report are presented below. The new material from the 2nd Quarter work activities then follows.

General Ethanol Production Background Information

First Generation Ethanol

First generation bioethanol is produced by fermenting plant-derived sugars to ethanol, using a similar process to that used in beer and wine-making. This requires the use of 'food' crops such as sugar cane, corn, wheat, and sugar beet. These crops are required for food, so if too much biofuel is made from them, food prices could rise and shortages might be experienced in some countries. Corn, wheat and sugar beet also require high agricultural inputs in the form of fertilizers, which limit the greenhouse gas reductions that can be achieved.

The complete processing of corn to ethanol is generally done at a single facility. Most of these ethanol plants are sited in Midwestern states, close to the farms where the corn is grown. Because of this close proximity, trucks are the predominate mode for the transportation of corn to ethanol plants. Once the corn is received at the plant it is stored in silos for up to 10 days until needed for ethanol production. Liquid transportation lines within the plant are usually above ground and are constructed from low alloy steel or stainless steel.

The ethanol production process involves milling, slurring, fermenting, distilling and purifying in a systematic manner to maximize production. At the present time, most ethanol in the US is produced from corn by either dry milling or wet milling processes. The U.S. is the top ethanol producer using corn as the feedstock and Brazil is the world's top ethanol producer using sugar cane as the feedstock. Vehicles in Brazil have been using 100 percent ethanol for decades.

The dry milling process reduces the particle size of the corn using a hammer mill. The particle size of the grain can influence ethanol yield so finely ground corn (1/8 to 3/16 inch) is used to maximize ethanol yield. Water is added to start leaching soluble protein, sugars, and non-starch bound liquids. Ammonia may be added to control pH.

Wet milling is different in that the corn kernel is separated into various fractions allowing production of other products besides ethanol. The cleaned kernel is soaked in water containing sulfur dioxide and lactic acid. After soaking, the germ is removed and the starch and protein separated by filtration and centrifugation. The starch is further purified by washing to remove protein.

After milling and slurring, starches from the corn are converted by amylolytic enzymes (enzymes capable of denaturing starch molecules) and heat into fermentable sugars (glucose). The fermentation is continued by the addition of *Saccharomyces cerevisiae* yeasts to produce low-grade ethanol. One by-product of the fermentation process is glycerol. Contamination by wild yeasts and microbes can be a problem, resulting in undesirable by-products such as lactic or acetic acid.

The low grade ethanol is refined by fractional distillation to produce ethanol that is 95.6% by volume (89.5 mole% or 190-proof). This mixture is an azeotrope with a boiling point of 78.1 °C and cannot be further purified by normal distillation. Desiccation, purification using molecular sieves, or azeotropic distillation is generally used to remove the remaining water.

Second Generation Ethanol

The goal of second generation biofuel processes is to extend the amount of biofuel that can be produced sustainably by using cellulosic or biomass comprised of the residual non-food parts of current crops. This includes stems, leaves and husks that are left behind once the food crop has been extracted, as well as other crops that are not used for food purposes, such as switch grass and cereals that bear little grain. Industry waste such as wood chips, skins and pulp from fruit pressing, and municipal solid waste are also used.

The major component of these cellulose-bearing materials is the fibrous material consisting of cellulose, hemicellulose, lignin, and other polysaccharides. While the refining process for cellulosic ethanol is more complex than that of corn-based ethanol, cellulosic ethanol yields a greater net energy and results in much lower greenhouse gas emissions.

The process to make ethanol from cellulosic material is not yet commercially viable from a economic perspective. Cellulose is very difficult to hydrolyze and the five-carbon sugars (pentoses) it produces are not fermentable with the yeasts normally used in ethanol production. Lignin, a partially polymerized phenolic resin, is a very undesirable contaminant.

One firm is working on techniques to make fermentation of cellulosic ethanol viable. Iogen Corporation is a privately held company, based in Ottawa, Ontario, Canada. Established in the 1970s, Iogen is one of Canada's leading biotechnology firms. They are an industrial manufacturer of enzyme products with a focus on products for use by the pulp and paper, textile and animal feed industries. Their specialty with respect to ethanol production is enzymatic fermentation. They are partnered with Shell, Goldman Sachs, Petro-Canada, and the Canadian government. With a \$15.8 million investment from Petro-Canada, Iogen built the company's pre-commercial demonstration plant located in Ottawa. The company has been producing cellulosic ethanol at its demonstration plant since 2004.

Other firms are developing very different techniques to make ethanol. Coskata headquartered in Warrenville, IL is producing ethanol via the fermentation of synthesis gas, or 'syngas' mainly made up of carbon monoxide and hydrogen. Their process uses proprietary microorganisms to convert the syngas to ethanol. Syntec Biofuel also uses syngas as their feedstock, but produces ethanol by passing the gas over

the catalysts in a fixed bed reactor, similar to the production process for methanol. The syngas used in both processes is generated through gasification of a variety of feedstocks.

Other research is focused on developing alternatives to the costly enzyme and yeast multi-step process. Mascoma Corporation in Lebanon, N.H., is working with a thermophilic bacterium. Oak Ridge National Laboratory researchers are studying *Clostridium thermocellum* which can both degrade the cellulose and ferment the resulting sugar. BC International is building a plant in Jennings, LA that uses genetically engineered *E. coli* bacteria to convert all forms of sugar.

Summary - Current/Common Liquid Fuels (Focused on Ethanol and Biobutanol) and What Feedstocks They Are Derived From

The common feedstocks for ethanol (biobutanol can be made from the same feedstocks as ethanol) were investigated and are summarized in Table 1 and Table 2 below.

Table 1 - Ethanol Feed Stocks (U.S. Production)

Ethanol (currently in production in U.S.)
Crops
Corn
Corn/barley
Corn/milo
Corn/wheat starch
Milo/wheat starch
Pearl millet (potential - SE US)
Waste Products
Cheese whey
Potato Waste
Wood waste
Waste beer
Beverage waste
Sugar cane bagasse
Brewery waste

Table 2 - Ethanol Feed Stocks (Non-U.S.)

Ethanol (Non-U.S.)
Sugarcane (Brazil)
Sugar beet
Wine (France/Italy)
Sake (rice wine - Japan)
Cassava (highest energy/acre - Tropical Areas)
Cellulosic biomass
Residues
Non-edible plant parts
MSW
Pulp/Paper industry waste
Wood waste
Forest residues
Dedicated crops
Grass
Short rotation trees

Biodiesel feedstocks currently in production in the U.S. are listed in Table 3.

Table 3 - Biodiesel (in U.S. Production)

Biodiesel (currently in production U.S.)
Oils
Soy
Canola
Cottonseed/soy
Cottonseed/soy/Canola
Palm
Animal Products
Yellow Grease
Animal Fat
Recycled oils and grease
Recycled Cooking oil
Waste Vegetable Oil
Multi Feedstock
Tallow/Yellow Grease/Soy/Poultry Fat
Soy/Animal Fats
Soy/Choice white grease
Cottonseed/animal fats
Plant Oils/Animal Fats
Soy/Poultry Fat

Overview of Current Transportation Methods for Ethanol

Ethanol has historically been shipped to markets via truck, rail and barge. It is stored at fuel terminals and blended with gasoline at or near the point of retail distribution. To sustain the market growth needed to meet the current suggested targets, infrastructure improvement should be considered for transporting biofuel and co-products to market.

Most ethanol is currently produced in the Midwest, but 80 percent of the U.S. population (and therefore implied ethanol demand) lives along its coastlines. Transportation factors to consider as ethanol production continues to expand include:

1. The capacity of the Nation's transportation system to move ethanol, feedstock, and co-products produced from ethanol.
2. The availability of corn close to ethanol plants (~ 10-15 miles).
3. The location of feedlots for use of co-products relative to ethanol producing areas.

In 2005, rail was the primary transportation mode for ethanol, shipping 60 percent of ethanol production (approximately 2.9 billion gallons of ethanol). Trucks shipped 30 percent and barges 10

percent. To date the growth of ethanol production and the construction and expansion of new plants have not been hampered by logistical concerns. Railroads kept up with ethanol growth in 2006. As ethanol production grew by 26 percent in 2006, railroads' shipments of alcohols (most of which is ethanol) increased by 28 percent.

This may not be the case in the future. All three modes used to transport ethanol—rail, barge, and truck—are at or near capacity. Total rail freight is forecast to increase from 1,879 million tons in 2002 to 3,525 million tons by 2035, an increase of nearly 88 percent.

Ethanol is shipped in the following containers.

1. Standard rail tank cars (approved for flammable liquids) - DOT 111A rail cars.
2. Standard gasoline tanker trucks (DOT MC306 Bulk Fuel Haulers). Truck drivers must have HAZMAT certification.
3. The main terminals served by barge include New York Harbor, Philadelphia, Baltimore, Providence, Chicago, New Orleans, Houston, Albany, and many others. Ethanol is typically shipped in 10,000–15,000 barrel tank barges. The number of ethanol plants located near a river facility, however, is relatively small.

There is one recently commissioned U.S. steel pipeline (Kinder Morgan) that is transporting fuel grade ethanol blended with gasoline from Tampa to Orlando. The presence of water is the greatest concern. Ethanol can strip impurities present inside multi-product pipeline systems resulting in undesirable contaminants. Another factor is the evidence that ethanol can induce stress corrosion cracking, especially at untreated weld joints. Liners, weld treatments, or coatings could help alleviate this.

Water contamination poses a problem in transportation of ethanol. A large investment in dehydrating and filtration/coalescing equipment would be required for any alcohol transportation by pipeline.

The high polarity of ethanol causes problems with certain elastomers also containing polar components. Nylon swells and loses tensile strength, similar to its behavior in water. Polybutene terephthalate also exhibits significant changes. ASTM D5798 specifies that unprotected aluminum must not be used as it will introduce insoluble aluminum compounds into the fuel. The effect is exaggerated by elevated fuel conductivity due to contact with nitrile rubber.

A detailed materials compatibility study for ethanol gathering lines will be completed as part of Task 3 of this project.

Ethanol Contaminant Information

To prevent diversion for human consumption, federal regulations require ethanol produced for fuel use to have a denaturant (usually gasoline) added before shipping. This is the source of the largest contaminant found in ethanol. The second largest would be inhibitors added to limit corrosion. These include ethyl tertiary butyl ether (ETBE), methyl tertiary butyl ether (MTBE), and various aliphatic ethers.

Other potential contaminants could be by-products of the production process and chemicals added to assist in milling, slurring, and fermentation. Some of these are mentioned in the previous sections on ethanol production. Other chemical reactions with deleterious effects are reactions of ethanol with phosphoric and sulfuric acid to form phosphate and sulfate esters. A complete dehydration with sulfuric acid could produce diethyl ether or ethylene.

The chemical structure of ethanol also offers some potential incompatibilities with other materials. Ethanol is made up of carbon, hydrogen and oxygen. The oxygen content provides no btu value. But it is this oxygen content that imparts very different properties to an alcohol, when compared to gasoline. The oxygen is present as a hydroxyl group (-OH), the same functional group found in water. Since the hydroxyl group is attached to the end of the molecule, it makes the alcohol molecule very polar. This also results in a high heat of vaporization as the molecule is very susceptible to hydrogen bonding, as opposed to very volatile gasoline.

Combustion of ethanol in air is presented in Equation 1 below.



Representatives from the US, Brazil and EU (Tripartite Task Force) met in 2007 to write a white paper on “Internationally Compatible Biofuel Standards”. The purpose was to compare biodiesel and biomethane standards from the three regions. An attempt was made to negotiate a harmonization of standards for future trade considerations.

The following conclusions were made:

1. Ethanol purity would be defined by the ethanol and water content.
2. Brazil and the US would define a minimum ethanol content of 98.0% by volume. The EU would use a lower limit of 96.8 %. The task force was hopeful that after further negotiations the EU would agree to the 98.0 % limit.
3. The EU limit for water content was more conservative than found in the US or Brazil.
4. Brazil has the lowest chloride limit. Inorganic chlorides contribute to fuel corrosiveness.

5. The EU is the only region having a phosphorus limit, based on data obtained from ethanol producers. Phosphorus may be an issue in cellulosic produced ethanol rather than corn produced ethanol. Phosphorus is a catalyst in the production of ethanol from petrochemical feedstocks.
6. Three parameters could not be compared because different test methodologies are used. These are residue by evaporation (gum), acidity, and pHe. It was hoped that an effort could be made that would lead to an agreement to standardizing test methods.
7. Brazil includes a specification for electrical conductivity (EC). It is felt that EC would be a quick test for purity.

Table 4 - Common Impurity Specifications

Parameter	Recommended Value	Notes
Color	Dyes Permitted	Ethanol may have a yellow color due to the presence of proteins
Heavier (C3-C5) alcohols	2% (ASTM, EU)	No Brazilian limit
Methanol	0.5% (US), 1.0% (EU)	No Brazilian limit
Hydrocarbons	3% (B)	Not specified in US and EU because it is a common denaturant.
Benzene	0.06% (CARB)	Denatured ethanol
Olefins	0.05% (CARB)	Denatured ethanol
Aromatics	1.7% (CARB)	Denatured ethanol
Gum or Residue from Evaporation	5 mg/100ml (US, B), 10 mg/100 ml (EU)	Consensus needed on technique
Sulfate	4 ppmw (US, B)	Problems of sulfate deposits. EU expected to harmonize
Total Sulfur	10 ppmw (US, EU)	Brazil to harmonize. Low level amounts of sulfur in all plant based materials.
Chloride	1 ppmw (ASTM), 25 ppmw (EU), 1 ppmw (B)	Very aggressive corrosion inducing contaminant. Auto industry wants 1 ppmw limit.
Phosphorus	1.3 mg/L (ASTM), 0.5 mg/l (EU)	Possible contaminant from fertilizer and nutrients used in growing or fermentation.
Copper	0.1 ppmw (EU), 0.07 (ASTM, B)	Intended to prevent contamination from Cu tubes and stills. Cu is an oxidation catalyst and will increase oxidation rates.
Lead	13 mg/L (ASTM)	
Sodium	2 ppmw (B)	Feedstock contamination
Iron	5 ppmw (B)	Feedstock contamination
Electrical conductivity	500 uS/m	Brazil feels this is a quick test for purity
Acidity	50 ppmw (ASTM), 70 ppmw (EU), 38 ppmw (B)	Complex acids may be produced from certain feedstocks. WU and Brazil feel parameter is important from a corrosion standpoint (specifically acetic acid).
pHe	6.5 – 9.0 (US), 6.0 – 8.0 (B)	Special meters and probes needed to be able to correlate data.

Note: Condensed from Dec 2008 white paper, CARB ethanol standards, and ASTM D5798 specifications.

A comparison of Ethanol versus Gasoline was conducted and the results are presented below in Table 5. Because there is an additional large body of knowledge of material (plastic) compatibility with gasoline, any similarities of Ethanol and Gasoline may be helpful during the material compatibility work activities of this project.

Table 5 - Properties of Ethanol versus Gasoline

	Ethanol	Gasoline
Molecular weight	46.07	100-105
Composition, by weight %		
Carbon	52.2	85-88
Hydrogen	13.1	12-15
Oxygen	34.7	0
Relative Density, 60/60°F	0.794	0.69-0.793
Density, lb/gal @ 60°F	6.61	5.8-6.63
Lower Heating Value		
BTU/lb	11,500	18,000-19,000
BTU/gal @ 60°F	76,000	109,000-119,000
Boiling point, °F	173	80-437
Freezing point, °F	-173.4	-40
Vapor pressure, psi	2.3	7-15
Water solubility, @70°F		
Fuel in water, volume %	100	negligible
Water in fuel, volume %	100	negligible
Viscosity		
@ 68°F	1.50	0.5-0.6
@ -4°F	3.435	0.8-1.0
Flash point, closed cup, °F	55	-45
Auto ignition temperature, °F	~793	~495
Flammability limits, volume @		
Lower	4.3	1.4
Upper	19.0	7.6
Latent heat of vaporization		
BTU/lb @ 60°F	396	~150
BTU/gal @ 60°F	2,378	~900
Stoichiometric air/fuel, weight	9.00	14.7
Moles product / moles charge	1.07	1.06
Moles product / moles O ₂ + N ₂	1.14	1.08

Ethanol Standards of Interest for Fuel Quality/Makeup

The primary standards related to ethanol fuel, quality, vehicle use, piping, and storage are listed below in Table 6. The "parent" standards (e.g., ASTM D4806) are highlighted in orange and drive many of the requirements for ethanol fuel and the components used in contact with it. The information in these standards will be coupled with the reference material presented above, the survey results, and testing of submitted samples to establish the boundaries of the constituent make-up of the ethanol fuel that would flow through gathering lines.

Table 6 -Ethanol Related Standards of Interest (Fuel Quality/Makeup)

Ethanol Fuel - General Standards/Specifications		
ASTM		
D4806	Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel	
D4814	Standard Specification for Automotive Spark-Ignition Engine Fuel	
D5798	Standard Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark-Ignition Engines	
WK 18986	New (in development) Specification for International Specification for un-denatured Fuel Grade Ethanol	
RFG Research Report D02: 1347	Research Report on Reformulated Spark Ignition Fuel	
EU		
pr EN 15376	Bioethanol - Auto-motive fuels - Ethanol as a blending component for petrol - Requirements and test methods	
RFA		
NACE TM-01-77	RFA recommends corrosion inhibitors and criteria falls to NACE standard	
Engine Fuel Quality		
NIST		
Handbook 130	Uniform Laws and Regulations in the Areas of Legal Metrology and Engine Fuel Quality	
Vehicular Fuel Systems		
SAE		
J1681	Gasoline, Alcohol, and Diesel Fuel Surrogates for Materials Testing	
J30	Fuel and Oil Hoses	
J312	Automotive Gasolines	
J1681	Gasoline, Alcohol, and Diesel Fuel Surrogates for Material Testing	
J2835	Recommended Practice for Flex Fuel Vehicles	

Pipeline and Piping Infrastructure; Transmission and Distribution

ASME

B31G	Manual for Determining Remaining Strength of Corroded Pipelines: Supplement to B31 Code-Pressure Piping
B31.1	Power Piping
B31.3	Power Piping
B31.4	Pipeline Transportation Systems for Liquid Hydrocarbons and Other Liquids
B31.8	Gas Transmission and Distribution Piping System
B31.8S	Managing System Integrity of Gas Pipelines
B31Q	Pipeline Personnel Qualification
API 579-1/ASME-FFS-1	Fitness For Service
PCC-1	Guidelines for Pressure Boundary Bolted Flange Joint Assembly
PCC-2	Repair of Pressure Equipment and Piping Standard
RTP-1	Reinforced Thermoset Plastic Corrosion Resistant Equipment
BPVC-IX	BPVC Section IX-Welding and Brazing Qualifications
BPVC-X	BPVC Section X - Fiber Reinforced Plastic Pressure Vessels (Boiler Pressure Vessel Code)
BPVC-XII	BPVC Section XII - Rules for Construction and Continued Service of Transport Tanks (Boiler Pressure Vessel Code)
B16.5	Pipe Flanges and Flanged Fittings: NPS through NPS24
B16.34	Valves -- Flanged, Threaded, and Welding End

Storage and Distribution

API

Standard 2610	Design, Construction, Operation, Maintenance, and Inspection of Terminal and Tank Facilities
Standard 650	Welded Steel Tanks for Oil Storage Publication
API 579-1/ASME FFS-1	Fitness For Service
TR 939-D	Stress Corrosion Cracking of Carbon Steel in Fuel-Grade Ethanol: Review, Experience Survey, Field Monitoring, and Laboratory Testing
RP 1004	Bottom Loading and Vapor Recover for MC-306 and DOT 406 Cargo Tank Motor Vehicles
RP 1007	Loading and Unloading of MC-306 and DOT 406 Cargo Tank Motor Vehicles
RP 1626	Storing and Handling Ethanol and Gasoline Ethanol Blends at Distribution Terminals and Service Stations
RP 1627	Storage and Handling of Gasoline-Methanol/Co-solvent Blends at Distribution Terminals and Service Stations
RP 1637	Color-Symbol System to Mark Equipment and Vehicles for Product Identification at Gasoline Dispensing Facilities and Distribution Terminals

Publication 1642	Alcohol, Ethers, and Gasoline Alcohol and Gasoline-Ether Blends
Publication Literature Review	Impact of Gasoline Blended with Ethanol on the Long-Term Structural Integrity of Liquid Petroleum Storage Systems and Components
Developing Standard MPMS Ch. 11.3	Ethanol and Gasohol Blends with Volume Correction Factors
NFPA	
NFPA 30	Flammable and Combustible Liquids Codes
NFPA 30A	Code for Motor Fuel Dispensing Facilities and Repair Garages
UL	
ANSI/UL 142	Steel Aboveground Tanks for Flammable and Combustible Liquids
UL 2080	Fire Resistant Tanks for Flammable and Combustible Liquids
UL 2085	Protected Aboveground Tanks for Flammable and Combustible Liquids
UL 2244	Aboveground Flammable Liquid Tank Systems
UL 2245	Below Grade Vaults for Flammable Liquid Storage Tanks

Completion of Draft Task 1 Survey

A draft survey was developed and sent to the Steering Committee for review and inclusion of topics and is included below.

Dear Survey Participant:

GTI is pleased to initiate the DOT PHMSA sponsored project, “*Feasibility of Using Plastic Pipe for Ethanol Low Stress Lines*”.

- > This research project will address the feasibility of using currently available polymer (thermoplastic or thermoset) pipe for new ethanol gathering systems.
- > A comprehensive study will be performed to assess the effects of ethanol blends on potential polymer pipe candidate materials, both polymeric and composites, as low cost, low maintenance alternatives to specially designed and joined metallic pipelines.

As an initial step, we have prepared a survey to ensure we are capturing and addressing the concerns of the ethanol industry. Part of its purpose is to survey ethanol producers and distributors about their experiences with trace constituents in ethanol, and what polymeric materials are in common use for transportation of ethanol. GTI would greatly appreciate your input through this survey.

All comments, information, and data received as a result of this survey will be kept under strict confidentiality. GTI would be pleased to provide a survey summary (with all specific company identifications removed) to any respondent once the results are tallied.

Please send (email is preferred) the completed survey by
Fri. March 27, 2009 to:

Ms. Karen Crippen, GTI

Email: karen.crippen@gastechnology.org

Fax: (847) 768-0970.

You may also call Ms. Crippen at: (847) 768-0604.

The *Renewable Fuels Association* (RFA) is on the steering committee for this project. If you have any concerns regarding this project or survey, you may contact:

Ms. Kristy Moore at (202) 289-3835, or by email at kmoore@ethanolrfa.org.

Thank you for your time to fill out this survey.

Andy Hammerschmidt
GTI Team Project Manager
andrew.hammerschmidt@gastechnology.org
847-768-0686

A. Questions Focusing on Additives and Trace Constituents in Ethanol

- Additives or trace constituents could have a potential deleterious effect on polymeric materials even at low concentration levels.
- The effect could be synergistic, depending on the specific chemical interaction.
- This part of the survey is designed to determine what constituents may be present, especially those compounds beyond what is typically monitored for.
- GTI would also like to analyze a representative selection of produced ethanol.
- Any published report of data obtained from this survey and from analysis of submitted ethanol samples will be completely confidential (anonymous). The different data sets would refer only to "Company A", "Company B", etc.

1. Appendix A of this survey contains a table listing the fuel components, additives, and impurities. [This is important information since these constituents may affect the physical/mechanical properties of some polymer pipe materials]. Please enter any available data you would be willing to share in the column labeled "Typical Concentrations".

> Entered data in Appendix A: ___YES ___NO.

2. If there are any *trace constituents* or *by-products* [not included in Appendix A] that might be introduced by the process of producing ethanol you are using, please list these directly below with any typical concentrations, if known [This is important for the same reasons as #1 above].

>

3. During processing, do you monitor (test for) for any trace constituents? (e.g., ASTM D4806 - Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel)?

If yes, please provide a typical chemical analysis data sheet (all responses will be kept confidential). [This is important for the same reasons as #1 above].

> Attached typical chemical analysis data sheet: ___YES ___NO.

4. Do you monitor for any constituents beyond what is listed in various specifications? If yes, please list below with typical concentrations.

>

5. What *specific* additives and concentrations of: corrosion inhibitors, denaturing agents, or drag reducing agents do you add to your ethanol product before it ships? [This information is important since these chemical agents may come into contact with the proposed plastic gathering lines if they are added to the ethanol prior to transport out of the facility].

>

6. At what point in the distribution system are the additives introduced or injected? [We are requesting the information for the same reason as #5 above].

>

7. Would you be willing to supply GTI with a physical sample (e.g., 500ml) of your ethanol? GTI would supply bottles, shipping containers, shipping instructions, and pay any shipping costs (all results would be kept confidential). [These samples will be analyzed for chemical constituents and the data will be used to validate and fill in the gaps of the data received from the survey and published literature/references].

If yes, please provide contact information below or contact Karen Crippen, GTI at (847) 768-0970.

>

B. Questions Focusing on Transportation of Ethanol

- *Knowledge of typical industry transportation practices is valuable supplementary information.*
- *In addition, any experience with material failures (of polymer or elastomeric components in contact with your ethanol stream) would supply important background data for the project scope.*
- *As mentioned previously, all responses will be kept strictly confidential.*

8. How is the ethanol transported (1) *within* the processing plant (and what materials are the transport vehicle/system made from) and (2) *from* the plant after processing (i.e., do you use pipelines, trains, tanker trucks, or barges)? Estimate the number of barrels per day and barrels per year (or gallons per year) that the plant produces. Also estimate the average distance of transport from the plant to the central distribution point, e.g., barge terminal. [This is important information since it will govern the size and flow rate of the required gathering lines].

>

9. What is the temperature of (1) the current ethanol storage tanks in the process plant; and (2) the ethanol product itself at the time of transport out of the plant? [This is important information since the temperature will affect the material compatibility of the plastic pipe material with ethanol and its additives].

>

10. What ancillary (secondary) components come into contact with the ethanol? Specific sizes are not necessary, but general information of valves, fittings, diaphragms, o-rings, seals, etc.

11. What polymer materials are the components mentioned above made from? [This is important to help to build a list of *materials* already being used in conjunction/contact with ethanol in the plant environment].

>

12. Do you find that your company must replace any polymeric or elastomeric components often (*prior* to failure)? [This could give an indication of what polymer/plastic/elastomeric materials are more susceptible to ethanol/additive degradation].

>

13. To what extent do you have issues with polymeric components actually failing in the plant? [This information is important for the same reason that was given in #12 above].

>

14. Are you concerned about issues such as contamination during transportation, phase separation, or corrosion? What *contaminants* might be introduced (e.g. additional water)? [As with the additives and trace constituents, it will be important to understand what other contaminants might come into contact with the polymer pipe material used for ethanol gathering lines].

>

Appendix A is on the next page.

Appendix A - Chemical Composition of Ethanol (Fuel Components, Additives, and Impurities)

<i>Parameter</i>	<i>Typical Concentration</i>	<i>Specification Limit in U.S.</i>	<i>Source</i>	<i>Concern</i>
Fuel Components				
Ethanol			Major constituent	
Methanol		0.5% (ASTM)	Fermentation by-product	Combustion
Heavier alcohols, glycerol		2% (ASTM)	Fermentation by-product	Combustion
Additives				
Benzene, Toluene, etc.		0.06% (CARB)	Denaturant	Combustion, environmental
Olefins		0.05% (CARB)	Denaturant	Combustion
Paraffins			Denaturant	Combustion
MTBE, ETBE			Corrosion inhibitor	
Impurities				
Water		1% (ASTM)	Processing by-product	Corrosion
Ammonia			Milling pH control	Precipitation with sulfate
Sulfate		4 mg/kg	Milling pH control, Impurity in feedstock	Precipitation, plugging
Chloride		42 mg/kg	Milling, Impurity in feedstock	Corrosion
Phosphorus, Nitrogen, Sulfur		10 mg/kg (CARB, sulfur only)	Impurity in feedstock, fertilizer, nutrients	Corrosion
Copper		0.07 – 0.1 mg/kg (ASTM)	Distillation processing	Oxidation catalyst
Lead			Distillation processing, Feedstock contamination	Environmental
Sodium, potassium, iron, calcium			Feedstock contamination	Corrosion, precipitation
Acetic, lactic, oxalate or other organic acids		0.005 – 0.007 % (ASTM)	Fermentation by-product	Corrosion
Protein			Fermentation by-product	Corrosion
Lignin			Incomplete hydrolyzation	Combustion
Enzymes			Fermentation additive	Environmental, cost
Glucose or other sugars			Incomplete fermentation	Environmental, cost
Diethyl ether			Production by-product	Environmental, corrosion
Ethylene			Production by-product	Combustion
Phosphate or sulfate ester			Production by-product	Combustion, corrosion

Ethanol Physical Sampling and Packing Protocol (for sample collection and submission)

A simple, but complete, sampling protocol was drafted to assist volunteer companies in properly sampling, packing, recording, and shipping sample shipments.

The protocol is presented directly below and will be provided to all companies that express interest in submitting ethanol samples to supplement the Task 1 research effort and survey results.

1. Sampling and Packaging Protocol

- 1.1. Samples of ethanol should be collected in clean borosilicate glass containers with Teflon lined caps. Fill the container completely, leaving little headspace. 500ml would be more than enough.
- 1.2. Attached the lid securely and seal around the rim with an elastomeric tape such as electrical tape.
- 1.3. Wrap sealed bottle with absorbent material.
- 1.4. Place wrapped bottle inside a plastic bag to contain the material should the bottle break.
- 1.5. Place inside paint can packaging.
- 1.6. Seal paint can by lightly tapping it lid down with a hammer.
- 1.7. Apply protective plastic over ring or clips, or seal metal drum. See Figs. 1 & 2.



Fig. 1. 4G box and paint can packaging system with plastic over ring and Styrofoam inserts.



Fig. 2. Paint can with clips.

- 1.8. Place can in box using Styrofoam inserts.
- 1.9. Fill out chain of custody record (see the full form located at the end of this document) and enclose it in the box or drum.
- 1.10. Seal box or drum and prepare shipping paperwork.

2. Filling out the Chain of Custody Record

- 2.1. **Company Name and Address of Sampling Site:** This field is used to specify where the samples came from. Fill in the name of your company and the complete address of the site where the samples were taken.
- 2.2. **Sampler:** The actual person who performed the sampling.
- 2.3. **Signature:** The actual person who performed the sampling.
- 2.4. **Sample:** How your company wishes to identify the samples. Can be any information or means of identifying the sample: alphanumeric combinations, etc.
- 2.5. **Date:** Date of sample collection.
- 2.6. **Time:** Time of sample collection.
- 2.7. **Sample Description:** Complete sample description (component type, etc.)
- 2.8. **Comments:** In the final column, please list any comments regarding the sampling process or the samples themselves that may be of use to the lab.
- 2.9. **Relinquished by:** When you relinquish custody of the sample. The FedEx shipping documentation is proof of when samples are received by FedEx, so the driver does not have to sign the form. It will be signed off as a final receipt when received in the laboratory.

3. Shipping

- The sample must be shipped as a hazardous material. Hazardous materials can be shipped either by ground shipment, or on a plane for overnight delivery. One will need a flammable liquid sticker. The proper UN shipping designation for ethyl alcohol (in the US) is UN1170. One must also be prepared to provide a copy of the Material Safety Data Sheet (MSDS) for your materials if FedEx requests it.
- Hazardous material shippers must be properly qualified through a FedEx sales representative before tendering hazardous material packages, there are no exceptions. There are classes that can be taken, and FedEx also offers an on-line hazardous materials training seminar.

The following material is directly excerpted from FedEx's web site:

[<http://www.fedex.com/us/services/options/ground/hazmat/packaging.html?link=4>]

- All hazardous materials must be packaged in United Nations Performance Oriented Packaging (UN POP).
- All packaging must meet the requirements set out in 49CFR 173.24 and 173.24a.
- Packaging that is not in new or "like new" condition will not be accepted by FedEx.
- In addition, the following requirements apply:
 - ⇒ All paint containers with friction-fitted lids must have a minimum of four clips, or a retaining ring, around the container lid.
 - ⇒ Hazardous materials cannot be shipped in any FedEx packaging.

- ⇒ When required, all Class 2 cylinders must be placed inside an overpack (outer package) marked “Inside packages comply with prescribed specifications.”
- ⇒ Fiberboard packaging must display a Minimum 200 lb. Bursting Test seal or 32 Edge Crush Test (ECT) seal. Gross weight cannot exceed the package specifications listed on the seal or our maximum weight limit of 70 lbs. (32kg) per package.
- ⇒ For packages weighing up to 20 lbs., use at least 32-edge crush test or 200-lb. bursting test corrugated containers.
- ⇒ For packages weighing 21–50 lbs., use at least 44-edge crush test or 250-lb. bursting test corrugated containers.
- ⇒ For packages weighing 51–70 lbs., use at least 55-edge crush test or 275-lb. bursting test corrugated containers.
- ⇒ FedEx Ground does not accept pails or drums over 8 gallons (32 liters). All pails or drums must be UN POP. FedEx will accept authorized pails or drums as single packaging.

NOTES:

- ⇒ This information is provided only as a guide. It assumes a representative sample can be obtained. It is the sampler’s responsibility to ensure a representative sample. Any historical information regarding the sample would aid us in better analyzing your sample. This would include previous results of laboratory or field screening analyses.
- ⇒ It is the sampler’s responsibility to ensure sampling is performed in a safe manner. Neither GTI nor any person acting on behalf of GTI assumes any liability with respect to the use of, or for damages resulting from the use of, any information presented in this procedure.

The chain of custody form is on the next page.

CHAIN OF CUSTODY RECORD

Company Name and Address of Sampling Site				Sampler Name																																																													
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Plans for Future Activity

Continue to work on Task 2 and Task 3 work activities with a focus placed on accelerating the specific items addressed in the paragraph above.

Respectfully Submitted,

Andy Hammerschmidt & Daniel Ersoy, GTI

End of Report